

THE USE OF THERMOGRAVIMETRIC ANALYSIS TO FOLLOW CHANGES DURING SHORT-CONTACT-TIME COAL LIQUEFACTION

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INTRODUCTION

The study of the chemical reactions involved in coal liquefaction is aided by elucidation of the processes occurring in the very early stages (low conversions), before secondary reactions of the products become significant. To this end, as reported in previous papers^{1,2}, we have developed a reactor system capable of carrying out liquefaction reactions at accurately known reaction times from as short as a few seconds (low conversions) to as long as 60 min or more. The analytical methods to monitor these reactions must provide sensitive measures of the coal conversion and product yield information. We have found thermogravimetric analysis (TGA) useful since it provides sensitive, rapid and reproducible results concerning the various weight loss changes that can be connected to the physical and chemical changes occurring during coal liquefaction.

Thermogravimetric analysis has other desirable features as well. First, only very small samples (about 30 mg) are required for each TG run. Second, by suitable adjustments in the work-up procedures and the TG running parameters, such as heating rate and atmosphere, thermogravimetric analyses yield important information concerning the reaction pathways.

It is to illustrate the usefulness of thermogravimetric analysis of coal liquefaction products that this paper is presented.

EXPERIMENTAL

Apparatus. The design and operation of the SCTBR reactor system have been described in detail previously¹. In brief, both the empty preheater and reactor are immersed in a Techne IFB-52 fluidized sand bath. They are brought up to the predetermined reaction temperature prior to the start of the reaction. High pressure nitrogen gas provides the driving force to deliver the reaction mixture of a coal-tetralin slurry from a small blow case into the empty reactor through the preheater tubing. Nitrogen gas is then bubbled through the reactor from the bottom to provide the agitation needed in the heterogeneous reaction system. The degree of agitation is controlled by the exit gas flow rate from the top of the reactor. The temperature of the reactant mixture (ca. 30 g) approaches the desired reaction temperature to within 5-8 °C of preset temperature during the transport process (approximately 0.3 seconds). This temperature is maintained within ± 2 °C during the experiment. At a preselected reaction time, high pressure nitrogen gas is again used to drive the reactor contents from the reactor into a cold receiver through the precooler. Both receiver and precooler are immersed in a water bath. Cooling of the product mixture to about 25 °C is achieved within 0.3 seconds.

Coal Liquefaction Runs. All reactions were run as mixtures of tetralin (T, the H-donor solvent) and coal (C) at ratio of T/C = 8. About 4 grams of coal were used for each reactor run together with added tetralin to make up the reactant slurry. The reactor runs are summarized in Table I. Hold up of material on the surfaces of the reactor, preheater, and precooler prevented complete recovery of the reaction products. However, the recoveries were high, and varied from about 80-90 wt%. The measure of conversion and subsequent analytical results were therefore based on representative aliquots.

Thermogravimetric Analysis. The thermogravimetric analyzer (TGA) was a Model 51 TGA (TA Instruments, New Castle, Delaware). A representative TG scan on the Illinois #6 coal from the Argonne Premium Coal Sample program is shown in Figure 1. The weight loss resulting from heating in nitrogen at 100 cm³(STP)/min with a heating rate of 10°C/min to 950°C and hold for 7 min at 950 °C defines the amount of volatile matter (VM). For this illustrative sample VM was 36.64 wt%. Further weight loss occurred at 950°C after the introduction of oxygen. This was due to the oxidation of the remaining combustible material, the so called "fixed carbon (FC)", in the char, which amounted to 48.42 wt% for the illustrative sample of Figure 1. The residue represents the ash content (14.94 wt%). Thus the two phases, i.e., 1) the heating rate to 950°C in nitrogen and hold for 7 min; and 2) the oxidation at 950°C, provided measures of VM, FC, and Ash, respectively. The experimental error for determination of these TGA characteristic variables (VM, FC, and Ash) is less than $\pm 2\%$ of the measured values.

Thermogravimetric analysis can also be run in a hydrogen atmosphere. This provides additional information regarding the structure of coal and liquefaction residue. However, it is required that nitrogen be introduced to replace hydrogen in the TGA system for about 10 min before the introduction of oxygen.

RESULTS AND DISCUSSION

Effect of Heating Rate and Atmosphere in TG Runs. The effect of heating rate on the DTG analysis of the Illinois #6 coal is illustrated in Figure 2. The two small peaks in the VM portion of the DTG curves gradually disappear as heating rate increases. This is due to the lower resolution of DTG profile at the higher heating rate. The DTG curves of the Illinois #6 coal in nitrogen and in hydrogen demonstrated in Figure 3 show the similar pyrolysis rate patterns. However, all three peak temperatures in the VM portion of TG pyrolysis in hydrogen are shifted to lower temperatures than those of TG pyrolysis in nitrogen.

Figures 4(a), 4(b) and 4(c) show plots of VM for Illinois #6, Utah Blind Canyon bituminous coals and Wyodak Black Thunder subbituminous coal, respectively. They were determined by TG pyrolysis in nitrogen and in hydrogen at heating rates varying from 10°C/min to 200°C/min. The heating rate had a strong effect on the volatile matter in nitrogen and in hydrogen. The VM yields in nitrogen (VM_{N_2}) increased with increasing heating rate until it leveled off at about 50 °C/min. This can be tentatively attributed to an unstable component in the coal when the volatile product is only slowly removed from the coal in nitrogen which results in free radical retrograde reactions and low volatile yields. The VM yields in hydrogen (VM_{H_2}) are always higher than those in nitrogen. This is because the presence of hydrogen in the TG pyrolysis apparently stabilizes or quenches these radicals to give the higher VM yields. VM_{H_2} decreased with increasing heating rate. This may be due to the longer pyrolysis times at the low heating rates. The different behavior in VM determined by TGA shown by the various coals in nitrogen and in hydrogen (see Figure 4) may represent an indication of the potential relative instabilities of the various coals. While the Illinois and Utah bituminous coals showed similar behavior with heating rate in hydrogen or nitrogen atmosphere, the Wyodak subbituminous coal showed only a small effect of heating rate on VM in the presence of nitrogen and quite a strong and reverse effect in the presence of hydrogen. Further research is being directed toward a better understanding of these phenomena.

Conversion Determination and Work-up Procedures for Coal liquefaction Runs. During coal liquefaction, the mineral matter of the coal primarily remains with the unconverted coal, and is essentially insoluble in the tetralin. The coal liquids, however, are largely extracted into the tetralin solvent, although some remain with the coal residue. This provides a means of measuring the conversion of the coal by determining the ash content of the residue when it has been washed free of the coal liquids. All the tetralin and tetralin-derived products must also be removed or an error in the conversion calculation will result. The conversion can be calculated using Eq. 1:

$$\text{Conversion} = \left(1 - \frac{X_o}{X}\right) \times 100 \text{ (wt\%)} \quad (1)$$

where X_o and X are the ash contents of the control sample and the coal liquefaction residue, respectively. The control sample is the original coal which is processed exactly as a liquefaction residue except running at room temperature.

After a liquefaction run, the product mixture is filtered and the residue washed with tetralin thoroughly and dried in a vacuum oven at about 105°C for 48 hours. A DTG curve for one of these samples is shown in Figure 5. Comparison of this curve with that of unreacted coal shows that there is an incomplete peak on the low temperature side of the principal VM peak in the coal residue. That this is due to the presence of residual tetralin is shown by a control sample treated by processing a tetralin-coal slurry through the reactor at room temperature. To measure the coal conversion accurately, the tetralin and the tetralin-derived materials as well as the coal liquefaction liquid products must be removed from the residue. The most satisfactory solvent we have found for this purpose is methylene chloride (see Figure 5). The tetralin peak disappears after methylene chloride washing. For this reason, we have adopted the work-up procedure including the methylene chloride treatment.

The conversion of Illinois #6 in tetralin vs. time at 390°C under 1000 psig nitrogen gas determined by Eq. 1 is illustrated in Figure 6. Within 30-60 seconds, the coal conversion has reached about 18 wt%. This rapid liquefaction may be resulted from the extraction of a soluble portion of coal into the tetralin. From the contact time of 1 min to 30 min, the coal conversion only increase about 19 wt% (reaching 37 wt%), probably due to the coal matrix itself being attacked. Finally, the coal conversion reached 47 wt% at 60 min.

Change of DTG Profiles with Conversion during Coal Liquefaction in Tetralin. Figure 7 shows DTG vs temperature curves for the residues of the Illinois #6 coal after liquefaction in tetralin at 390 °C under 1000 psig nitrogen at selected times. The two small peaks in the VM portion gradually disappear. Such chemical changes have been supported by previously observed changes in the total oxygen content and hydroxyl content^{3,5} of the

coal during the early stages in coal liquefaction.

Change of Volatile Matter in N_2 and in H_2 with Conversion during Coal Liquefaction in Tetralin. Interesting insights into the coal structure and the coal liquefaction process can be obtained by running thermogravimetric analyses in nitrogen and in hydrogen at various heating rates on the samples taken at various reaction times. The coal liquefaction process, even at low conversion, greatly changes the TG behavior of the partially reacted coal residue. Figure 8 shows an example of the VM determined by TG pyrolysis in nitrogen and in hydrogen at various heating rates for the liquefaction residue of the Illinois #6 coal reacted in tetralin under 1000 psig nitrogen gas at 390°C for 30 seconds. The VM_{N_2} no longer shows the strong sensitivity to heating rate. Furthermore, it decreased with increasing heating rates. This suggests that the unstable component of the coal may have been stabilized in the very early stage of the liquefaction process.

SUMMARY AND CONCLUSIONS

Thermogravimetric analysis provides various weight changes in coal residua arising from coal liquefaction and these reveal significant information concerning the underlying chemical and physical processes.

A workup protocol including the methylene chloride washing to eliminate the error due to the presence of tetralin and/or coal liquids has been devised which is being used along with TGA to determine liquefaction conversion.

Interesting differences have been observed in the three Argonne Premium Coal Samples (Illinois #6 bituminous coal, Utah Blind Canyon bituminous coal, and Wyodak Black Thunder subbituminous coal) studied by running TGA at different heating rates and in nitrogen or hydrogen atmosphere. These experiments suggest the presence of an unstable component in the coal or coal-derived liquid which is rapidly removed or stabilized by very short contact time under liquefaction conditions.

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References

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Table I Illinois #6 Coal Liquefaction Runs

Sample	Contact time min	T/C (wt)	Temperature °C	Recovery wt%
DOE001	15.00	8	15	78%
DOE012	0.17	8	390	86%
DOE015	0.50	8	384	92%
DOE016	0.75	8	385	89%
DOE017	1.00	8	386	88%
DOE021	5.00	8	387	87%
DOE013	10.00	8	390	82%
DOE009	30.00	8	390	85%
DOE010	60.00	8	390	81%

Sample: Illinois #6
 Size: 44.7080 mg
 Method: DDE Coal Liquefaction
 Comment: 10 °C/min to 950 °C, N₂, 100 ml/min (after drying)

TGA

File: C: ILL6N2.016
 Operator: Keyu Wang
 Run Date: 19-May-94 16:59

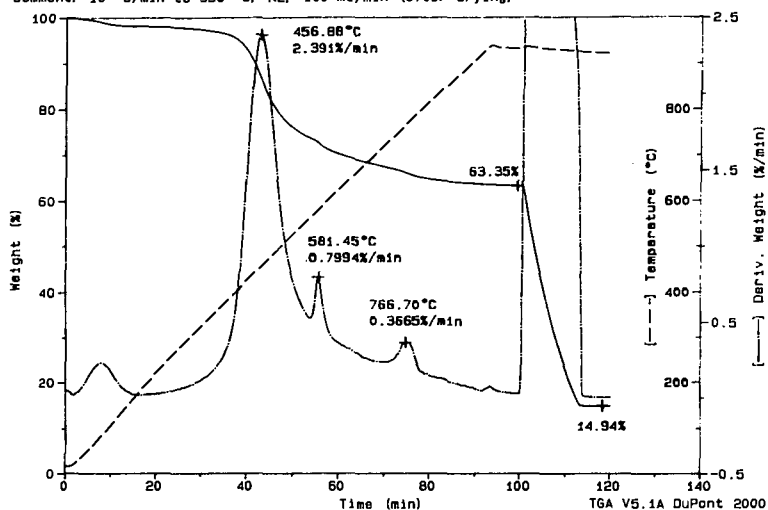


Figure 1. A TG scan on the Illinois #6 coal

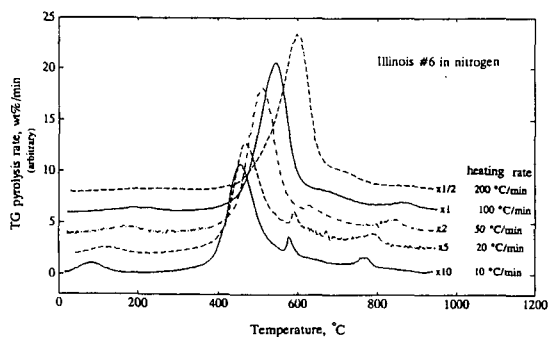


Figure 2. Effect of heating rate on DTG of the Illinois #6 coal pyrolysis in N₂

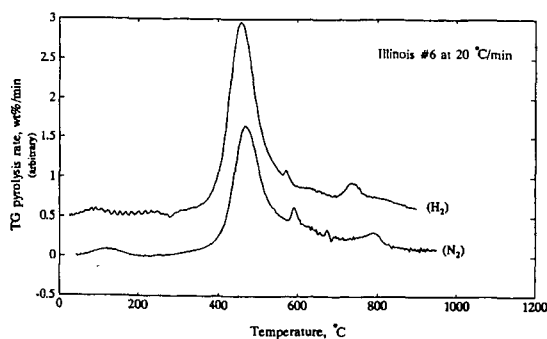


Figure 3. Effect of gas atmosphere on DTG of the Illinois #6 coal pyrolysis at heating rate of 20 °C/min

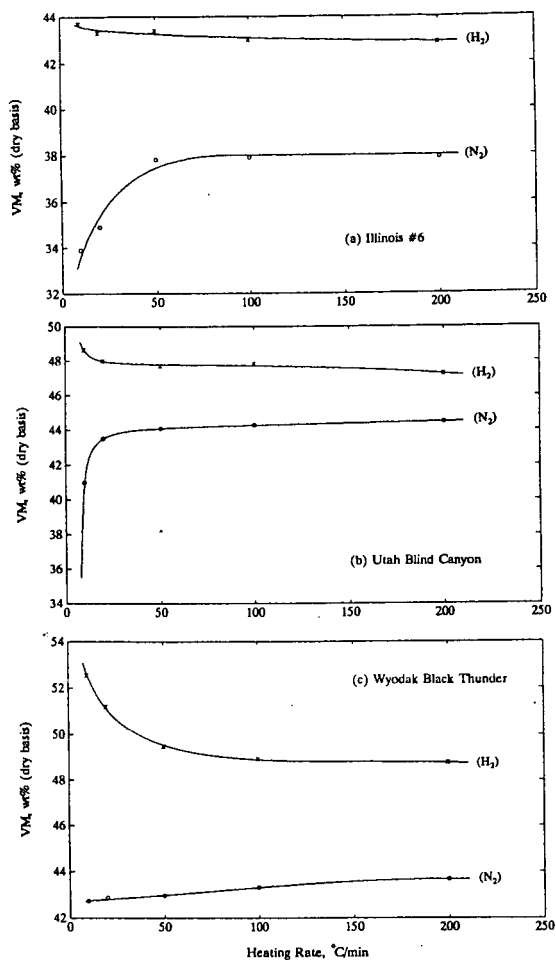


Figure 4. Effect of heating rate on the VM yields determined by TG pyrolysis in N_2 and in H_2

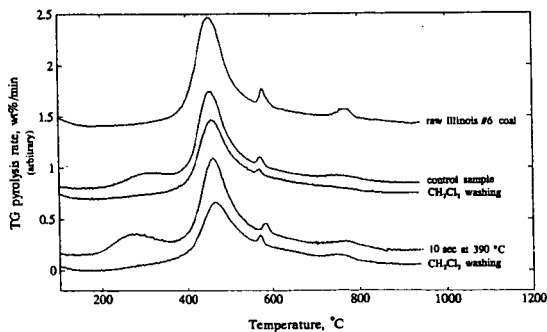


Figure 5. Disappearance of the incomplete peak on the low temperature side of the principal VM peak due to the presence of residual tertalin in the control sample and the reacted solid residue by methylene chloride washing

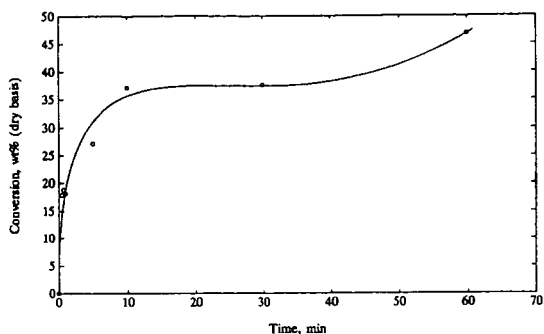


Figure 6. Kinetics of the Illinois #6 coal liquefaction in tetralin (1000 psig N_2 gas; 390 °C; T:C = 8:1)

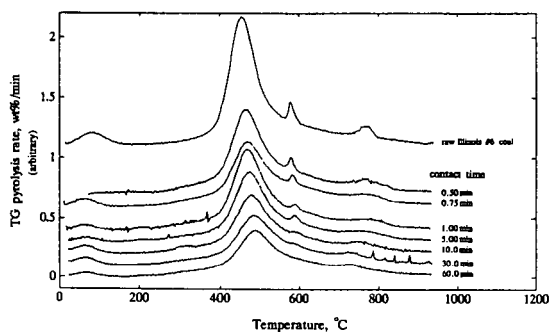


Figure 7. DTG profiles for residues of the Illinois #6 coal after liquefaction in tetralin at the selected contact times (TG scan at 10 °C/min in N_2 ; liquefaction run at 390 °C under 1000 psig N_2 with T:C = 8:1)

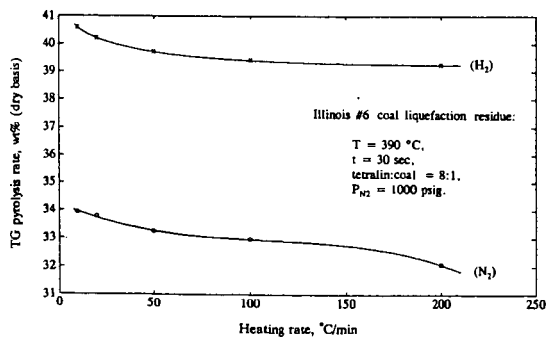


Figure 8. Effect of heating rate on VM yields of Illinois #6 coal liquefaction residue determined by TG pyrolysis in N_2 and in H_2